

1047,069



# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Blends of Polyamide Resins with Acrylic Resins

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel compositions comprising blends of polyamides and acid-containing methyl methacrylate based polymers.

It has long been a desired object in the plastics art to modify the intrinsic properties of one polymeric substance by blending it with another having different properties. However, in this field blending has proved extremely unsuccessful since even polymers, which are extremely closely related chemically, are generally incompatible. One approach to the solution of this problem has been to provide vigorous mixing. However, such blends remain heterogeneous mixtures of such coarse structure that, even after vigorous mixing in the melt, the solidified compositions are relatively weak and readily exfoliate, and in no way approach the desired average of properties of the several components.

In accordance with the present invention, useful blends of polyamide resins and methyl methacrylate based polymers are obtained by intimately melt blending from 1 to 99% by weight of a polyamide thermoplastic resin with from 99 to 1% by weight of a polymethyl methacrylate resin having copolymerized therein from 1 to 20 equivalents of an ethylenically unsaturated carboxylic acid per 100 moles of total monomers.

The blends of the present invention are two-phase systems, and have a characteristic

and attractive milky white appearance. In the case of the blends containing high proportions of the methyl methacrylate polymer, the blends are somewhat translucent. Although the blends of this invention are two-phase in character, the dispersion is exceptionally fine, and the two phases can scarcely be distinguished under a high powered optical microscope. Rough measurements of the particle size show that the size of the dispersed phase is of the order of about 1 micron. This fine dispersion may be achieved by simple melt mixing procedures which are well known in the art such as milling with a Banbury mill or by joint extrusion of the polymeric components. Extraordinary measures are not required. It has been found that a single extrusion mixing operation produces the optimum dispersion, and no improvement in homogeneity or significant change in physical properties is effected by re-extrusion one or more times.

The dispersions are extremely stable and the material may be maintained as a quiescent melt for extended periods of time without any observable separation of the two phases.

The polyamides which may be employed in the practice of this invention are well known in the art and embrace those compositions commonly designated as nylons. Among these polyamides may be mentioned those described in United States Patents 2,071,250 and 2,071,251, both issued to W. H. Carothers on February 16, 1937, and U.S. 2,130,523 and 2,130,948, both issued to W. H. Carothers on September 20, 1938, which are derived from dibasic acids such as oxalic, succinic, adipic, suberic, and sebacic acids, and diamines such as hydrazine, ethylene diamine, pentamethylene diamine, hexamethylene diamine, decamethylene diamine

or tetramethylene diamine, including those polyamides derived from cyclic diamines or diacids such as the polyamides from di(4-aminocyclohexyl) - methane (British Specification No. 619,707), or poly(p-phenylene terephthalamide) or poly(m-phenylene isophthalamide/terephthalamide); the polyamides derived from monoamino - monocarboxylic acids or from their cyclic lactams (U.S. Patent No. 2,071,250 issued to W. H. Carothers on February 16, 1937, British Specifications No. 461,236 and 535,421) e.g., the polyamides of 6-aminocaproic acid, 11-aminoundecanoic acid, or 12-aminostearic acid, including the polyamides of alpha-amino acids, such as leucine, beta-phenylalanine or 1-aminocyclohexane carboxylic acid, the copolyamides from diamines, dicarboxylic acids, and amino acids, e.g., those of British Specification No. 548,263.

Preferred polyamides are polyhexamethylene adipamide (66 nylon), polyhexamethylene sebacamide (610 nylon), polycaprolactam (6 nylon), and copolymers which may be designated 66/610 nylon, 66/6 nylon, and the like.

Mixtures of the above polyamides may also be employed in this invention.

The polyamides should preferably have a molecular weight of at least 2000, i.e., they should be high molecular weight polymers. On the other hand, in view of the substantial increase in viscosity which may be attained by blending according to the present invention, it is by no means essential that the molecular weight of the polyamides should be sufficiently great of themselves to yield a commercially useful thermoplastic material.

With regard to the acidic methyl methacrylate polymers which are employed as the second component of the blend, these should desirably contain at least 50 mole per cent of methyl methacrylate copolymerized therein and preferably at least 85% by weight of methyl methacrylate. Small proportions of other vinyl monomers may be incorporated into the polymers including, for example, ethyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, styrene, alpha methyl styrene, p-phenyl styrene, butadiene, isoprene, vinyl acetate, vinyl butyrate, vinyl methyl ether, vinyl ethyl ether, vinyl isopropyl ether, isobutylene, trichloroethylene, vinyl chloride and ethylenically unsaturated polyesters.

The acidic component of the polymer should provide from 1 to 20 carboxylic acid groups per 100 moles of the total monomers. Alpha - beta ethylenically unsaturated carboxylic acids may be successfully employed, including mono and dibasic acids such as acrylic acid, methacrylic acid, alpha-ethyl acrylic acid, itaconic acid, maleic acid, fumaric acid, and half-esters of ethylenically unsaturated dicarboxylic acids, preferably with lower ali-

phatic alcohols, such as methyl hydrogen maleate and ethyl hydrogen fumarate. Many other acidic monomers can be employed, as will be apparent to those skilled in the art. In general, the acids should contain from 3—20 carbon atoms.

The copolymerization of the aforesaid monomers may be accomplished by methods which are well known to those skilled in the art. Generally, these methods involve mixing the monomers and activating the polymerization with a free-radical forming catalyst such as a peroxide, e.g., benzoyl peroxide, tertiary butyl hydroperoxide or an azo compound, such as azo-bis-isobutyronitrile. Ionizing radiation, ultraviolet light or the like, may also be used to initiate the polymerization. Telogens, e.g., n-butyl-mercaptan, may be employed to control the molecular weight of the methyl methacrylate copolymer which should generally have an inherent viscosity measured in chloroform or a like suitable solvent of at least 0.25 and preferably at least 0.5 in order to obtain the optimum properties for the blends of this invention. The higher viscosity methacrylate polymers are particularly desirable when the methacrylate polymer is the major component of the blend.

In the case of blends prepared with a higher melting polyamide such as polyhexamethylene adipamide (66 nylon), it has been found particularly advantageous to employ copolymers containing from 1 to 20 equivalents of methacrylic acid per 100 moles of the total monomers, from 1 to 15 weight per cent of ethyl acrylate and the balance methyl methacrylate. These copolymers give blends with polyamides which exhibit superior toughness to blends made with simple copolymers of methyl methacrylate and methacrylic acid, particularly when high concentrations of the methacrylate polymers are employed.

As has been indicated hereinabove, the blends are readily made with mixing equipment now in general use by simply mixing the desired proportions of the component polymeric substances. As stated above from 1 to 99% by weight of the methacrylate polymer may be present in the blend. However, in the range between 50% and 70% by weight of the acrylic resin, the toughness and the tensile strength of the resultant blends are inferior to those properties in blends containing greater and lesser amounts of the methyl methacrylate polymers. It is believed that in the blends containing more than about 50% by weight of the polyamides, the polyamide is the continuous phase, and that above about 70% by weight of the methyl methacrylate polymer, the methyl methacrylate polymer provides the continuous phase. The somewhat inferior properties of the intermediate compositions are therefore attributed to the change from the polyamide as the con-

tinuous phase to the acrylic resin as the continuous phase. Compositions containing from 5 to 50% by weight and from 70 to 90% by weight of the methyl methacrylate polymers are preferred.

With regard to the acid concentration in the methacrylate polymers, it has been found that compositions which employ methacrylate polymers having more than 20 equivalents of carboxylic acid groups per 100 moles of total monomer are intractable materials which are not suitable for molding. On the other hand, while blends of polyamide resins with minor amounts of non-acidic polymethyl methacrylate can be made, they have inferior properties to the blends made with the acid containing methacrylate polymer, the inferiority being increasingly apparent as attempts are made to blend higher proportions of the polymethyl methacrylate in the polyamide.

The blends of the present invention are useful as thermoplastic molding compositions. The blends having the methyl methacrylate polymers as the continuous phase exhibit a stiffness which is substantially independent of the polyamide concentration, and substantially equal to that of the parent methacrylate polymer, but are substantially tougher than unmodified polymethyl methacrylate. Blends having the polyamide component as the continuous phase, on the other hand, have substantially the stiffness of the unblended polyamide when dry, but retain a much greater degree of stiffness on exposure to humid atmosphere than the unblended polyamides.

Fillers, antioxidants, thermal stabilizers, pigments, and the like may be employed. Particularly attractive compositions are found with the blends of this invention and inorganic fibrous fillers such as asbestos or glass fibers, which should be employed in amount of from 10 to 50% by weight in admixture with from 90 to 50% by weight of the polyamide-methyl methacrylate polymer blend. Preferred compositions containing such fillers have the polyamide as the continuous phase, i.e., from 60% to 90% by weight of the blend should be a polyamide. Surprisingly, although the blends are themselves somewhat inferior to the polyamide in tensile strength, when mixed with glass fibers, for example, the

tensile strength is superior to equivalent glass-filled polyamide compositions in the absence of the methyl methacrylate polymers.

While this invention has been described in detail with respect to copolymers containing principally methyl methacrylate as the methacrylate component, it will be realized that useful blends of a similar character can be obtained by replacing the methyl methacrylate wholly or partly by a different alkyl ester of methacrylic acid, for example, n-butyl methacrylate or isobutyl methacrylate or a mixture thereof.

This invention is further illustrated by the following Examples which are, however, intended to illustrate and not to limit the scope of this invention. RH in certain of the following Examples stands for Relative Humidity.

#### EXAMPLE 1

An acid-containing methyl methacrylate polymer was made by polymerizing a mixture of 89 parts by weight (88.3 mole per cent) of methyl methacrylate, 6 parts by weight (5.9 mole per cent) of ethyl acrylate and 5 parts by weight (5.8 mole per cent) of methacrylic acid, together with about 130 parts by weight of water, 700 parts per million by weight of n-butyl mercaptan as telogen, and with 0.12% by weight of azo-bis-isobutyronitrile as catalyst by heating the mixture to 105°C. under autogeneous pressure. The total polymerization time was half an hour. The resultant polymer had an inherent viscosity, measured in chloroform at 20°C of 0.62. Titration indicated the presence of about 4 mole per cent of methacrylic acid in the polymer.

The methyl methacrylate polymer was then extruded and cut into molding granules, after which it was compounded with varying amounts of "Zytel" 101 (trade mark), a commercial polyhexamethylene adipamide (66 nylon), having an inherent viscosity of 1.25 measured in m-cresol at 25°C. by mixing the methacrylate polymer molding granules with the polyamide molding granules and extruding with a 2" Royle extruder at a temperature of 280°C.

The resultant blends and their properties (measured as molded) are shown in Table I.

TABLE I

Example	Wt. % Polyamide	Tensile Strength kg/cm <sup>2</sup>	Elongation %	kg/cm <sup>2</sup> Flex Modulus	cm/kg Izod Impact
Polyamide control	100	900	21.0	31,100	9.55
Methacrylate polymer control	—	657	2.9		3.46
I a	90	877	15.0	31,800	7.47
b	70	857	4.0	31,700	6.78
c	60	836	4.0	32,000	7.61
d	50	765	2.8		5.40
e	40	605	1.9		3.18
f	30	725	2.7		5.12
g	25	688	2.4		3.46
h	20	809	3.1		5.12
i	10	767	2.9		4.01

5 The rheological properties of the blend (a) were measured using a constant rate rheometer. At a shear stress of  $10^5$  dynes/cm<sup>2</sup> and at 280°C. the methyl methacrylate polymer had a melt viscosity of  $7.6 \times 10^3$  poise. The parent polyamide had a melt viscosity of  $1.3 \times 10^3$  poise measured under the same condition. The addition of only 10% by weight of the methacrylate polymer to the polyamide raised the melt viscosity to  $1.3 \times 10^4$  poise, greater than that of the methyl methacrylate polymer alone.

10 The blends (b) and (g) were re-extruded twice, and the physical properties were re-measured. Within the limits of experimental error, the physical properties were identical with those recorded in Table I.

All of the blends had an attractive, white, opaque appearance and gave milky melts. Examination of thin microtomed sections under the microscope showed that an extremely fine dispersion had been achieved, the size of the particles in the dispersed phase being of the order of 1 micron.

#### EXAMPLE 2

The same methacrylate polymer employed in Example 1 was blended with "Zytel" 211, a commercial polycaprolactam (6 nylon), in varying amounts. The physical structure and appearance of these blends were indistinguishable from those of Example 1. The physical properties of the blends are recorded in Table II.

TABLE II

Physical Properties of Blends of Polycaprolactam  
with an Acidic Methyl Methacrylate Polymer

Physical Property	"ZYTEL" 211 Control	40% "ZYTEL" 211 Ex. 2 a	30% "ZYTEL" 211 Ex. 2 b	20% "ZYTEL" 211 Ex. 2 c
Tensile Strength kg/cm <sup>2</sup>				
Dry	724	900	879	907
50% RH (1)	688	649	678	731
100% RH	338	397	431	511
Elongation %				
Dry	243	19	9	4
50% RH (1)	274	106	90	26
100% RH	187	121	100	21
Flex Modulus, kg/cm <sup>2</sup>				
Dry	17,200	30,200	31,200	31,200
50% RH (1)	7,580	20,200	22,700	24,800
Izod Impact (2) cm/kg				
Dry	36.0	4.36	2.90	2.62
50% RH (1)	(No break)	6.63	3.46	2.21

(1) Conditioned in boiling solution containing 125 grams of potassium acetate per 100 grams of water.

(2) Measured on 1.25 cm × 0.3 cm specimen with molded notch.

## EXAMPLE 3

A monomer mix was made up as follows:

- 5 Methyl methacrylate  
95 wt. % (94.2 mole %)  
Methacrylic acid  
4 wt. % (5.8 mole %)  
n-butyl mercaptan telogen  
700 parts/million,

10 and polymerized in aqueous dispersion following substantially the procedure set forth in Example 1.

The resultant polymer had an inherent viscosity of 0.62.

15 Twenty parts by weight of the above methyl methacrylate polymer was blended

with 80 parts by weight of "Zytel" 31, a commercial polyhexamethylene sebacamide (6,10 nylon), using a 5 cm twin screw extractor extruder, and an extrusion temperature of 240°C. The melt had a characteristic milky appearance and extruded readily to a smooth surface strand which was chopped to form molding granules.

The tensile strength of injection molded samples of the blend was 562 kg/cm<sup>2</sup> with an 8% elongation (dry). The Izod impact strength (cut notch) at 73°C. was 0.4 (dry). In 50% RH conditioned samples, the tensile strength was 520 kg/cm<sup>2</sup> with a 15% elongation at break and the Izod impact strength was 10.5 cm/kg.

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**EXAMPLE 4**

A methyl methacrylate polymer was prepared using the following recipe

5	Methyl methacrylate	
	92 parts by weight	
	Ethyl acrylate	
	6 parts by weight	
10	Methacrylic acid	
	2 parts by weight	
	n-butyl mercaptan telogen	
	700 parts/million	

The mix was polymerized in aqueous dispersion using substantially the conditions employed for Example 1. Blends were prepared by extruding 25 parts of the above methacrylate polymer with 75 parts of polyhexamethylene adipamide and 70 parts of the above polymers with 30 parts of polyhexamethylene adipamide. The blends were well dispersed and the melt was stable on heating at 280°C. Solid bars prepared by injection molding had an attractive appearance but "blushed" on blending.

**EXAMPLE 5**

A methacrylate polymer was made, following the procedure set forth in Example 1 and

employing the following mix:

Methyl methacrylate	
91 parts by weight (90.2 mole %)	
Ethyl acrylate	
4 parts by weight (4.0 mole %)	30
Methacrylic acid	
5 parts by weight (5.8 mole %)	
n-butyl mercaptan telogen	
700 parts/million	35

The inherent viscosity of the resultant product was 0.6 measured in chloroform at 20°C.

A blend was made consisting of 63 parts by weight of polyhexamethylene adipamide, inherent viscosity 1.25 measured at 25°C. in m-cresol, 7 parts by weight of the above methyl methacrylate polymer and 30 parts by weight of chopped glass fibers (approximately 6 mm lengths) which had been sized with a silane size. For comparison, 30 parts by weight of the glass fibers were blended with 70 parts by weight of the same polyhexamethylene adipamide. Both blends were melt mixed by passing them through a 5 cm twin screw extractor extruder.

The physical properties were measured and are set forth in Table III.

TABLE III

Physical Properties of Glass-Filled Polyhexamethylene Adipamide  
with and without Methyl Methacrylate Additives

Property	Glass-filled polyhexamethylene adipamide	Glass-filled polyhexamethylene adipamide with methacrylate polymer
Flex modulus, kg/cm <sup>2</sup>		
Dry	66,700	76,700
50% RH	39,200	48,900
Tensile strength, kg/cm <sup>2</sup>		
Dry	1,100	1,260
50% RH	725	850
Elongation, %		
Dry	3.6	3.5
50% RH	10.1	6.2
Heat Distortion temp. °C.		
kg/cm <sup>2</sup>	>200° C.	>200° C.
kg/cm <sup>2</sup>	>200° C.	>200° C.
Color	Olive Drab	Gray

#### WHAT WE CLAIM IS:—

1. A thermoplastic composition which comprises a blend of from 1 to 99% by weight of a polyamide thermoplastic resin and from 99 to 1% by weight of a copolymer of methyl methacrylate and an ethylenically unsaturated carboxylic acid in the proportions of from 1 to 20 equivalents of the acid to 100 moles of total monomers.
2. A thermoplastic composition according to claim 1 which contains from 5 to 50 or from 70 to 90% by weight of the methyl methacrylate copolymer.
3. A thermoplastic composition according to claim 1 or 2 in which the polyamide is polyhexamethylene adipamide, polyhexamethylene sebacamide, polycaprolactam, a copolymer thereof or a mixture of the polymers and/or the copolymers.
4. A thermoplastic composition according to any of claims 1 to 3 in which the polyamide has a molecular weight of at least 2000.
5. A thermoplastic composition according to any of claims 1 to 4 in which the methyl methacrylate copolymer contains at least 85% by weight of methyl methacrylate.
6. A thermoplastic composition according to any of claims 1 to 5 in which the methyl methacrylate copolymer also contains from 1 to 15% by weight of ethyl acrylate.
7. A thermoplastic composition according to any of claims 1 to 6 in which the unsaturated carboxylic acid is methacrylic acid.
8. A modification of the thermoplastic composition according to any of the preceding claims in which the methyl methacrylate is wholly or partly replaced by a different alkyl ester of methacrylic acid.
9. A thermoplastic composition according to claim 1 substantially as herein described in any of the Examples.
10. A composition which comprises a thermoplastic composition according to any of claims 1 to 9 together with from 10 to 50% by weight on the total composition of an inorganic fibrous filler.
11. A composition according to claim 10 in which from 60 to 90% by weight of the thermoplastic composition is a polyamide.

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A. A. THORNTON & CO.,  
Chartered Patent Agents,  
Northumberland House,  
303—306, High Holborn, London, W.C.1.  
For the Applicants.

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